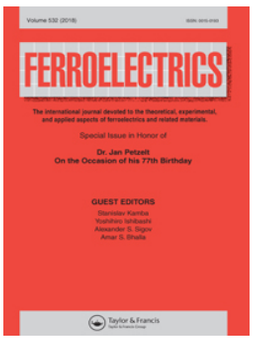

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Ultrafast polarization switching of $(BaSr)TiO_3$ thin film by a single-period terahertz pulse in a vicinity of phase transition

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ABSTRACT

We report here an experimental and theoretical study on ultrafast switching of dielectric polarization in $(Ba_{0.8}Sr_{0.2})TiO_3$ thin films by a strong electric field of a nearly single-cycle THz pulse at different temperatures. Optical second harmonic generation (SHG) is used as a probe of the polarization in the terahertz pump-optical probe experiment. We describe an approach to interpretation of SHG response from the ferroelectric polydomain film excited by a short electric field pulse. We show that dielectric polarization induced by the THz field decreases while approaching the Curie temperature. Simulations with the help of the Duffing equation reproduce the experimental observations.

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KEYWORDS
Terahertz; nonlinear optics; polarization switching

1. Introduction

The unique feature of ferroelectrics is their ability to switch dielectric polarization allowing them to serve as key components in ferroelectric memories, actuators and electro-optical modulators. The speed of switching determines the maximum operational frequency of such devices. While for memories and actuators, polarization reversal and creation of remnant polarization is important, for modulators dynamic high frequency polarization modulations is the main operation parameter.

Recently, new THz techniques were developed for both investigation and operation of the order parameter in ferroelectrics. THz spectroscopy extended significantly the knowledge in the area of ferroelectric phase transitions and ferroelectric switching. Significant contribution to this area has been made by J. Petzelt [1] who showed that THz spectroscopy is a very sensitive tool to study soft and central modes in thin films on substrates. Regarding the materials studied in this paper ($BaTiO_3$), he showed that central mode and soft mode coexist in the THz range and that the soft phonon mode softens only partially [2,3].

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THz pump-probe techniques, along with characterization on ultrafast time scale give an instrument to operate dielectric polarization in a controlled manner. Electric filed can be applied to ferroelectric material in a contact-free fashion using freely propagating nearly single cycle THz pulse. The detection of the pulse-induced changes can be carried out by optical [4,5] or by X-Ray diffraction techniques [6,7]. In optical detection, time domain reflectivity (transmission) or polarization rotation are studied. For ferroelectrics, optical second harmonic generation (SHG) is widely used as optical probe(see for review [8,9]) as well. It is sensitive to spatial inversion (SI) and provides information on structural (ferroelectric) phase transition and polarization switching [10,11].

Optical excitations can be also used for polarization switching. The idea [12] is to use coherent phonons excitation by impulsive Raman scattering analogously to magnon excitation in magnetic materials [13]. However, contrary to magnetization switching, the polarization switching has not achieved in this way in spite of extensive studies [14–16].

In this paper, we present experimental results revealing ultrafast dynamic response of the polarization in ferroelectrics to the electric field of a nearly single-cycle THz pulse. In order to check applicability of the Landau theory for ultrafast processes, the studies were performed at different temperatures, including the range in the vicinity of phase transition. The model based on the Duffing equation for forced oscillator with the coefficients derived from the Landau theory was used and showed a reasonable agreement with the experimental results.

2. Experiment and results

We studied ferroelectric 400-nm thick film of barium strontium titanate $(Ba_{0.8}Sr_{0.2})TiO_3$ (BST) (111). The Curie temperature for this composition is about 350K. The film was fabricated by RF-sputtering of stoichiometric polycrystalline target on MgO(111) substrate. The details of the sample preparation are described in Ref. [17]. Pure MgO substrate was measured in our experiments as well in order to isolate the signal from the film. The sample was put in the heater with optical window operating from room temperature up to 350 K.

The sample was firstly characterized by X-Ray diffraction technique, which showed (111) epitaxial structure. Secondly, SHG microscopy was used to visualize domain structure. Each spot in Figure 1a corresponds to single domain, which is confirmed by azimuthal dependences of SHG intensity (Figure 1b). The latter shows the presence of 120 degrees domains only. 180 degrees domains are undistinguishable in this plot. The corresponding model of domain structure is shown in Figure 1c along with direction of electric field vector of THz wave.

No any electrodes were attached to the sample, and electric field was applied remotely by single-cycle THz pulses experiment as shown in Figure 2. The details of the THz generation process and characteristics of the terahertz pulse are described elsewhere [18]. The pump beam was characterized by terahertz time-domain spectroscopy (TDS) similar to that described in Ref. [19]. The peak electric field of the THz pulse in the present experiment was 0.8 MV/cm, and the duration was 1 ps. The result of the THz field excitation was probed by a Cr:Forsterite laser with the central wavelength of

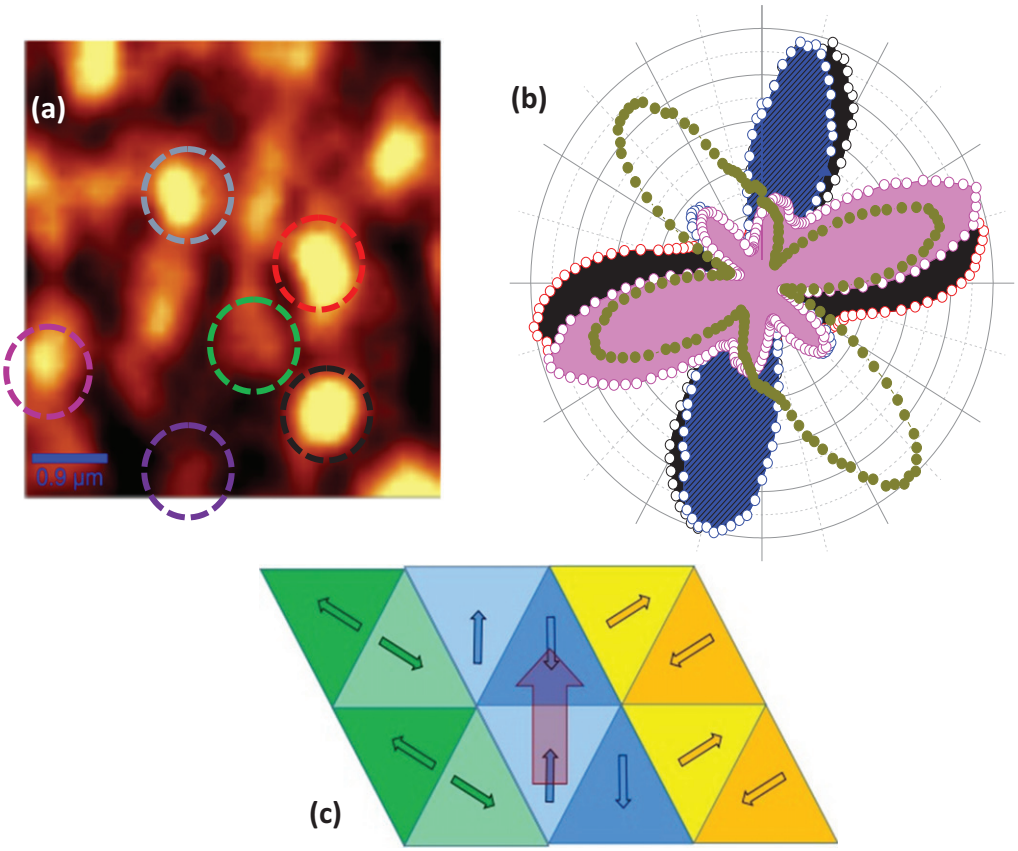

Figure 1. (a) SHG map; (b) azimuthal SHG dependences for differet domains (the color of the curve coincides with the color of the circle; (c) domain configuration schematic model regarding to THz field direction (big arrow); middle-size arrows show direction of polarization in each domain.

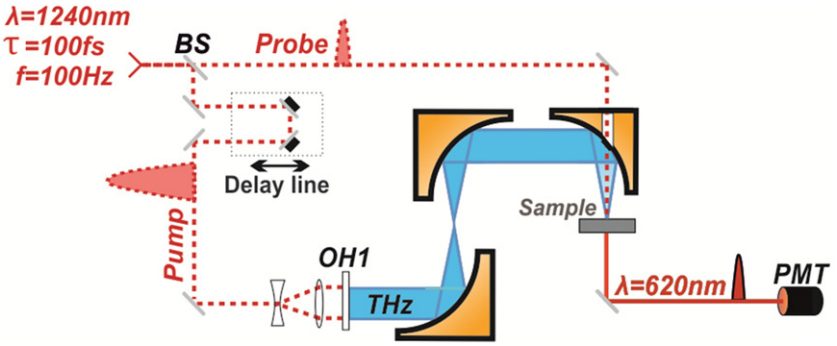

Figure 2. Schematic of experimental set-up.

1240 nm, 100 fs pulse width, 100 Hz repetition rate. THz wave was focused by parabolic mirrors onto a spot of about 800 μm in diameter.

The optical probe was focused by a lens into the spot of 200 μm in diameter. The pump and probe beams were at normal incidence. The time delay τ_d between the THz-

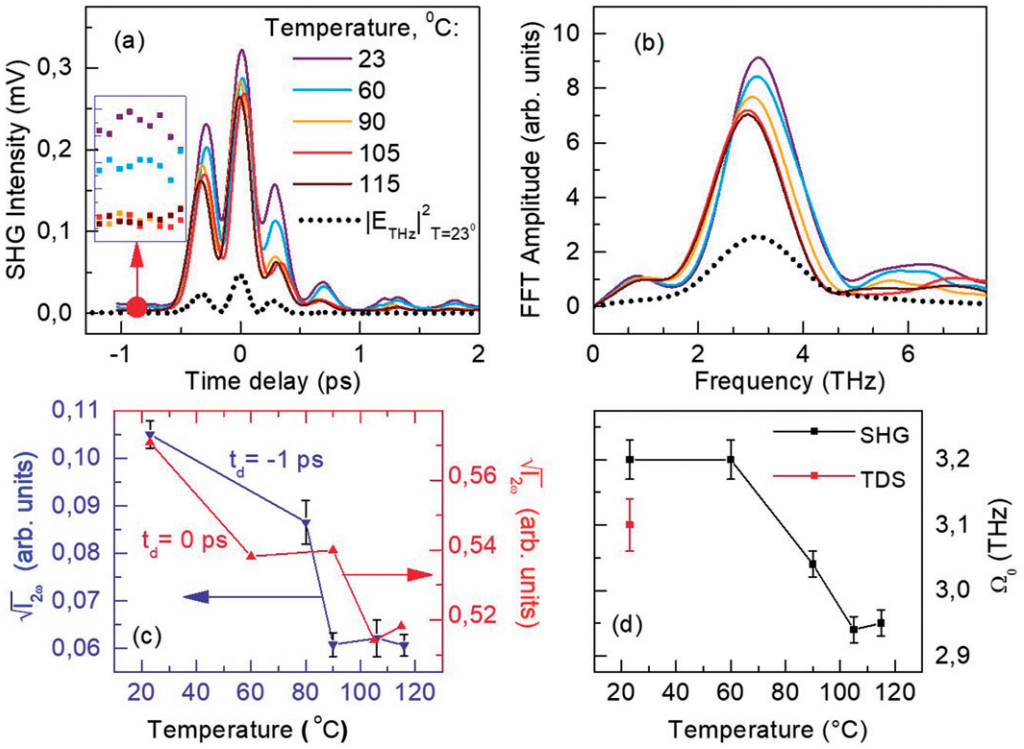

Figure 3. (a) Experimental time-domain SHG intensity at different temperatures; dashed line – w0, the shape of the square of input THz electric field measured as square of TDS signal; (b) Fourier spectra of time-domain signals presented in (a); (c) temperature dependences of SHG intensity measured at $t_d = -1$ ps (prior to THz pulse excitation) and at the second (main) maximum of time-domain SHG dependence ($t_d = 0$ ps); (d) temperature dependences of the central frequency of SHG response; the central frequency for TDS squared at 23 °C.

pump and the optical-probe pulses was changed by a delay line. Zero time delay was defined as the maximum in the TDS or SHG signal, respectively.

Optical second harmonic generation (SHG) was used as a measure of ferroelectric polarization. Second harmonic light was generated with the central wavelength of 620 nm. Details of the SHG detection could be found in Ref. [20] and [21]. All experiments were performed in a dry atmosphere (humidity less than 0.5%). Polarization of all waves was kept horizontally (parallel to one of the polarization directions). The square of THz pulse profile is shown by dashed line in Figure 3a.

Figure 3a shows time dependence of the SHG intensity $I_{2\omega}(t)$in BST film under excitation with a single-cycle THz pulse having the peak electric field amplitude of 500 kV/cm. The measurements were performed at different temperatures. A temperature increase results in a decrease of the total SHG intensity before and after arrival of the THz pulse (inset in Figure 3a shows the temporal dependence of $I_{2\omega}(t)$prior to THz pulse) as well during the action of the THz field. Qualitatively the temporal shape of the SHG signal is similar to the square of THz pulse profile shown by dashed line in Figure 3a. However, while the minima in $(E_\Omega(t))^2$ dependence equal zero, the minima in $I_{2\omega}(t)$ dependence do not reach zero at any temperature. Fourier spectra of $I_{2\omega}(\Omega)$

for all temperature dependences are plotted in Figure 3b. With a temperature increase, a decrease of the Fourier amplitudes is observed. Additionally, slight shift of the spectral maxima positions can be found.

3. Discussion

Under THz excitation, $I_{2\omega}(t)$ can be written as [20]:

$$I^{2\omega}(\mathrm{t}) = I_{bg}^{2\omega} + \alpha\Big(P_0 + P(E_\Omega(\mathrm{t}))\Big)^2, \tag{1}$$

where $I_{bg}^{2\omega}$ is the incoherent component of the unswitchable part of the second harmonic signal; $P(E_\Omega)$ is the ferroelectric (switchable) polarization, which depends on the electric field of the THz pulse; P_0 is remnant polarization i.e. unswitchable polarization; α is the proportionality coefficient, which is determined by the Fresnel factors and the nonlinear optical susceptibility.

If $I_{bg}^{2\omega} \to 0$ and $P_0 < P(E_\Omega(\mathrm{t}))$ (that is the case of our experiment), then $I^{2\omega}(\mathrm{t}) \propto P(E_\Omega(\mathrm{t}))^2$. In a linear range of $P(E_\Omega(\mathrm{t}))$ one can assume quadratic dependence of $I^{2\omega}(E_\Omega)$.

Temperature dependences of the related parameters are plotted in Figure 3c–d: square root of SHG intensity as the measure of dielectric polarization

$$\sqrt{I_{2\omega}(t_d = -1ps)} = P_0, \tag{2a}$$

$$\sqrt{I_{2\omega}(t_d = 0)} = P_{\max}, \tag{2b}$$

and positions Ω_0 of maxima of SHG THz spectra obtained by the fitting of each spectrum by the Gaussian function. Figure 3c shows that both remnant P_0 and maximal P_{max} polarizations decrease monotonically with the temperature increase. The value of Ω_0 decreases slightly. The shift of Ω_0 towards lower frequency exceeds strongly the error bar, but is much smaller than the width of the maxima. For room temperature, the value of Ω_0 obtained from the SHG spectrum is lower than the appropriate frequency obtained from the TDS spectrum.

Presently, several attempts to describe ultrafast polarization switching in ferroelectrics using nonlinear Duffing oscillator have been performed [22–24]. In the following we would like to use the same approach to calculate SHG temporal response of BST film to THz pulse.

The SHG requires additional discussion. (111)-BST films consist of three 120-degrees domain net (see Figure 1b). Polarization of one third part of these domains is parallel to THz electric field (we will call them "parallel" and denote as "||"), polarization of the rest of domains is oriented 120° regarding to THz electric field orientation (we will call them "120-degree" domains and denote as "±120"). Each part of this net is splitted into 180-degrees domains (domain size [8] is much smaller than the probe beam diameter). Before excitation, the domains mutually almost compensate each other (noncompensated domains give a nonzero signal prior to the THz pulse application). 120-degree parts of the net will be described by the Duffing equation with reduced (by $\cos(120) = 0.5$) electric field amplitude input pulse and reduced (by $\cos(120) = 0.5$ as well) generated SHG field. 180-degrees domains will be described by different initial conditions for the Duffing equation. Due to nonlinearity of the Duffing equation both

different initial conditions and reduction of the driving force results in strongly different solutions.

As a result, we have six equations for $Q^+(t)$ and $Q^-(t)$:

$$\begin{aligned}\ddot{Q}(z,t)+2\Gamma\dot{Q}(z,t)+aQ(z,t)+bQ(z,t)^3=\beta E_{THz}(z,t);\{Q_1(t=0)=Q_0,Q_2(t=0)=-Q_0\}\\ \ddot{Q}(z,t)+2\Gamma\dot{Q}(z,t)+aQ(z,t)+bQ(z,t)^3=0.5\beta E_{THz}(z,t);\{Q_{3,6}(t=0)=Q_0,Q_{4,5}(t=0)=-Q_0\}\end{aligned} \tag{3}$$

According to the Landau theory [25], the parameters come from potential energy $U(Q)=aQ^2+bQ^4(a/b=40$ at room temperature as in Refs. [26] and [27]), $a=-a_0\sqrt{(Tc-T)}$), decay constant $\Gamma=1/\tau_{dec}$). External force is $F=E_{THz}/e$, where THz electric field is approximated as $E_{THz}(t)=A\exp(-4(t-t_0)^2/\tau^2)\mathrm{sinc}(2\pi t+\varphi)$, τ is the width of the THz pulse, φ is the initial phase, e is the electron charge.

SHG field $E^{2\omega}(t)$ is proportional to the dielectric polarization $P(t)$[28,29] that based on Eq. (2) is

$$E^{2\omega}(t)\propto P(t)=e\sum_V((Q_1+0.5\cdot(Q_3+Q_5))+\gamma\cdot(Q_2+0.5\cdot(Q_4+Q_5))), \tag{4}$$

summation holds over the probe illuminated volume V, coefficient 0.5 comes from the projection of the domain orientation over the field direction, and γ is a measure of domains noncompensation, the requirement of which is a consequence of the experiment (nonzero SHG intensity for unexcited film). The measured SHG intensity is electric field squared: $I^{2\omega}=(E^{2\omega}(t))^2$.

Figure 4 shows the results of the calculations. Qualitatively, the temporal dependences of SHG intensity are similar to the experimental ones: each consists of one big central maximum and lower side-maxima. The difference (if compared with the experimental results) can be noticed in the shift of the central maximum regarding to zero time delay (overlap position) and zero value of SHG intensity in the first minimum. Spectral dependences of the calculated SHG are wider than the experimental ones.

Remnant polarization P_0 was calculated using Eq. (4). Since for $t=0$, coordinate Q holds initial condition, then P_0 is determined by coefficient a analogously to classical static conditions [25]: $P_0\propto\sqrt{-\frac{a}{b}}=\sqrt{-\frac{a_0(T-T_c)}{b}}$. The correspondent dependence $P_0(T)$ is shown in Figure 4c, triangles. At the same time, the temperature of the maximal value of calculated polarization P_{max} deviates significantly from the square root dependence (see Figure 4c, squares). It should be emphasized that contrary to remnant polarization, the maximum polarization decreases with the temperature increase but does not approaches zero at the Curie temperature. In order to trace the temperature dependence of the calculated frequency of the maxima in SHG spectra, the spectra were treated analogously to experimental spectra. Appropriate temperature dependence of the obtained frequency, $\Omega_0(T-T_C)$ is plotted in Figure 3d. Contrary to experimental dependence, in the calculated one the frequency Ω_0 increases with temperature, however the range of frequency variation is even smaller than that of the experimental value of Ω_0.

It is important to note that during the action of the THz pulse, the ions of the medium move under action of the driving force. If the frequency of the soft mode is in the spectrum of the THz pulse, after the action of the THz pulse the ions will oscillate

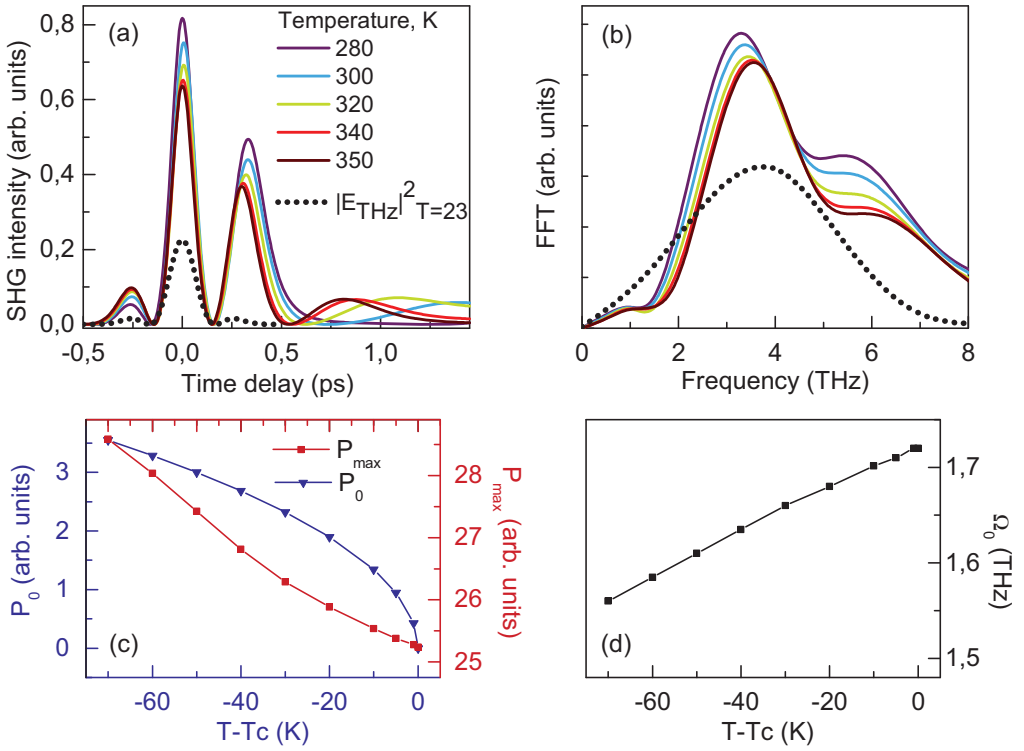

Figure 4. Calculated SHG temporal dependences for different temperatures (a) and their Fourier spectra (b); calculated temperature dependences of remnant polarization P_0, maximal polarization P_{max} (c) and Ω_0 as position of maxima in spectral SHG dependence (d).

at the frequency of the soft mode similarly to the case of free induction decay in Nuclear Magnetic Resonance. If the frequency of the soft mode is outside the spectrum of the excitation, manifestation of the soft mode in such an experiment is not expected.

Two items have to be emphasized. The first one is devoted to the theoretical calculations. The temporal shape of the SHG intensity generally does not coincide with the temporal shape of the input field. The reason is that we consider several unit cells with different initial conditions. As we showed in Ref. [30], this gives different (oscillating) solutions for 180 degrees domains. The same holds for 120-degrees domains. Thus, we have six different solutions, which are not harmonic. Their superposition (the final ESHG) produces quite complicated temporal dependence, and with the spectrum that does not coincide with the spectrum of initial pulse (See Figure 2d–e in Ref. [30]). This also confirms that within the THz pulse it is improperly to look for the soft mode within the duration of the THz pulse.

The second important item is the difference between minimal values of the SHG intensity in the experimental and calculated temporal dependences. In the theoretical dependences in the minima the SHG intensity equals zero. In the experimental dependences the SHG intensity does not reach zero at any time delay (within the pulse duration). For thick samples, such an effect may arise due to propagation effects [31]. This is not the case of the BST films. To explain the observed effects, further development of

the mode is required. One of the possibilities is modification of the Landau-Khalatnikov equation (for instance, for such ultrafast processes coefficients a and b may become time-dependent). But even within the standard Duffing equation, the observed effect may arise due to the reasons of nonlinear optics due to possible slight dephasing of ion movements.

4. Conclusions

We studied SHG response of ferroelectric thin film committing temperature induced phase transition on ultrashort and intensive terahertz electric field. SHG as a measure of dielectric polarization reveals switching of ferroelectric polarization within the time duration of the pulse. Even very strong near-resonant THz field does not excite soft mode and SHG intensity approaches its initial value instantly after the pulse end. The SHG response follows the square of THz field almost completely with only deviation in the points with zero THz field.

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